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(54) Title: <b>METHOD FOR THE PREPARATION OF A REINFORCED POLYMER COMPOSITION WHICH CONTAINS FIBRILS OF A CRYSTALLINE POLYOLEFIN</b>			
(57) Abstract			
<p>The invention relates to a method for the preparation of a reinforced polymer composition which contains fibrils of a crystalline polyolefin having a weight-average molecular weight (Mw) of at least <math>5 \times 10^5</math> kg/kmol, particles of the crystalline polyolefin being converted into fibrils in a matrix material which is immiscible with the crystalline polyolefin, in which method the crystalline polyolefin has a maximum stretch ratio of at least 20 and the conversion to fibrils takes place at a temperature below the melting point of the crystalline polyolefin. The invention also relates to reinforced polymer compositions obtainable by this method.</p>			

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METHOD FOR THE PREPARATION OF A REINFORCED  
POLYMER COMPOSITION WHICH CONTAINS FIBRILS  
OF A CRYSTALLINE POLYOLEFIN

The invention relates to a method for the preparation of a reinforced polymer composition which 5 contains fibrils of a crystalline polyolefin having a weight-average molecular weight ( $M_w$ ) of at least  $5 \times 10^5$  kg/kmol, particles of the crystalline polyolefin being converted into fibrils in a matrix material which is immiscible with the crystalline polyolefin.

10 A method of this type is disclosed in DE-A-2418803. According to this "Offenlegungsschrift" a reinforced polymer composition is obtained in which fibrils of the crystalline high molecular weight polyolefin impart an increased ultimate tensile strength to the polymer composition.

15 Preferably, the fibrils have a diameter of less than  $5 \times 10^{-5}$  m and a length of from  $2 \times 10^{-3}$  to  $20 \times 10^{-3}$  m. The polymer composition has a homogeneous appearance on the macroscopic scale. The polymer composition can be processed to give films, sheets, tapes, sections and the like.

20 The temperature at which fibrils are formed in the polymer composition lies in the region of the melting point and preferably somewhat above the melting point of the crystalline polyolefin. According to the examples for polyethylene this temperature is approximately 150°C. If no 25 special measures are taken, relaxation occurs after the formation of the fibrils and the fibrils can lose their elongated shape. An example which is given of such a measure is the cooling of the polymer composition under tension to a temperature below the melting point of the crystalline 30 polyolefin. A disadvantage of this measure is that it

demands accurate control of the processing conditions. Moreover, some relaxation of the fibrils still always occurs.

The aim of the invention is, therefore, the preparation of a polymer composition which is reinforced by fibrils and has a high ultimate tensile strength, the formation of fibrils taking place in an easily controllable manner and relaxation of fibrils which have formed being prevented.

This aim is achieved in that, in the method according to the invention, the crystalline polyolefin has a maximum stretch ratio of at least 20 and the conversion to fibrils takes place at a temperature below the melting point of the crystalline polyolefin.

Surprisingly, polymer compositions prepared according to the invention have an appreciably higher ultimate tensile strength and modulus of elasticity than the known polymer compositions. The fibrils in the polymer composition have an ultimate tensile strength ( $\sigma$ ) of at least 1 GPa and a modulus (E) of at least 20 GPa.

Crystalline polyolefin having a maximum stretch ratio of at least 20 is already known per se, for example from US-A-4769433. This patent describes the stretching of polyethylene of very high molecular weight which has never been dissolved or melted ("virgin PE") and has been prepared by polymerisation at relatively low temperatures. This type of crystalline polyolefin with a high maximum stretch ratio has a low entanglement density.

The "virgin" polyethylene as prepared according to US-A-4769433 can be further characterised by the difference between the initial melting enthalpy of a sample and the melting enthalpy which is obtained when the sample has been completely melted and then solidified again. The difference (fall) in melting enthalpies is preferably at least 10% of the initial melting enthalpy and in particular at least 20%. Moreover, the crystallinity of the polyethylene just mentioned is high, at least 77% and preferably more than

80%.

Polyolefin having a high maximum stretch ratio can also be obtained from polyolefin having a normal or low maximum stretch ratio via the so-called "gel route". In this procedure the polyolefin having a normal or low maximum stretch ratio is dissolved at elevated temperature in a suitable solvent, such as, for example, decalin, paraffin oil or paraffin wax, the solvent being removed after cooling, for example by evaporation or extraction. The resulting material can be ground, preferably cryogenically, after which further processing can take place in the method according to the invention. polyolefin having a high maximum stretch ratio, prepared in this way, does not always have to meet the crystallinity and melting enthalpy difference criteria given above.

The maximum stretch ratio of the crystalline polyolefin is at least 20, preferably at least 40 and in particular at least 80.

The maximum stretch ratio is determined as follows: a layer of polyolefin powder 2 mm thick is compressed in a circular mould having a diameter of 5 cm for 5 minutes at room temperature under a weight of 50,000 kg. The circular film obtained is then post-pressed at a temperature of 10°C below the melting temperature of the polyolefin (130°C for UHMWPE) for 10 minutes under a weight of 100,000 kg in a plane press. A dumbbell-shaped test piece with a length between the shoulders of 10 mm is punched from the film thus obtained. This test piece is stretched in a Zwick 1445 Tensile Tester at a temperature of 130°C, at a rate of 10 mm/min until the test piece breaks. The maximum stretch ratio is determined as the quotient of the length of the section of the test piece between the shoulders when break occurs in the test piece and the length of said section before stretching (10 mm).

Melting temperatures  $T_m$  and melting enthalpies  $\Delta H$  are determined by differential scanning calorimetry (DSC) using a scanning rate of 5°C/min and an initial temperature

of 40°C. The DSC measurements were carried out, using a Perkin Elmer DSC-7, on samples weighing  $4 \times 10^{-3}$  g.

5 Calibration of the DSC measurements was carried out using Indium ( $T_m = 156^\circ\text{C}$  and  $\Delta H = 28.45 \text{ J/g}$ ). The melting enthalpy  $\Delta H$  is determined from the surface area beneath the melting curve. Crystallinities (%) are calculated by dividing the melting enthalpy  $\Delta H$  of the sample by the melting enthalpy of 10 100% crystalline polymer. For polyethylene it is assumed that the  $\Delta H$  for 100% crystalline polymer is 293 kJ/kg.

The weight-average molecular weight  $M_w$  is determined using the methods known for this purpose, such as gel permeation chromatography (GPC) and light scattering. 15 For polyethylene having a weight-average molecular weight  $M_w$  of at least  $5 \times 10^5 \text{ kg/kmol}$ ,  $M_w$  is calculated from the intrinsic viscosity (IV), determined in decalin at 135°C. The said weight-average molecular weights of 0.5 and  $1.0 \times 10^6 \text{ kg/kmol}$  correspond to an IV in decalin at 135°C of 20 5.1 and 8.5 dl/g respectively, in accordance with the empirical relationship:

$$M_w = 5.37 \times 10^4 [\text{IV}]^{1.37}$$

Preferably, the weight-average molecular weight  $M_w$  of the crystalline polyolefin is between  $1 \times 10^6$  and 25  $10 \times 10^6 \text{ kg/kmol}$ .

According to the invention, crystalline polyolefin is understood to be a homopolymer or copolymer of an olefin, having a DSC crystallinity of at least 30%. Preferably, the DSC crystallinity is at least 50%.

30 Examples of polyolefins to be used according to the invention are polyethylene, polypropylene, polybutene and poly-4-methylpentene-1.

Advantageously very high molecular weight linear polyethylene (ultra high molecular weight polyolefin or 35 UHMWPE) can be used in the method according to the invention. UHMWPE is here understood to be linear polyethylene having fewer than 10 side chains per 1,000 carbon atoms and preferably having fewer than 3 side chains per 1,000 carbon atoms, or a polyethylene of this type which

also contains minor amounts, preferably less than 5 mol%, of one or more other alkenes copolymerised therewith, such as 5 propylene, butene, pentene, hexene, 4-methylpentene, octene, etc., which polyethylene or copolymer of ethylene has a weight-average molecular weight of at least  $5 \times 10^5$  kg/kmol. The polyethylene can also contain minor amounts, preferably at most 25% by weight of one or more other polymers, in particular an alk-1-ene polymer, such as polypropylene, polybutadiene or a copolymer of propylene with a minor amount of ethylene.

Polyolefins that are used according to the invention can, for example, be produced with the aid of a Ziegler process or a Phillips process using suitable catalysts and under known polymerisation conditions. See for instance P. Blais and R. St. John Manley in Journal of Polymer Science Part A-1, Vol. 6, 291-331 (1968).

The polyolefin can also contain non-polymeric materials, such as solvents, waxes and fillers. The amount of these materials can be up to 60% by volume relative to the polyolefin.

The matrix material which is used according to the invention and the crystalline polyolefin must be thermodynamically immiscible under the conditions under which the crystalline polymer is converted to fibrils. The processing temperature of the matrix material must be below the melting point of the crystalline polyolefin. Preferably the matrix material is so chosen that the adhesion between the matrix material and the crystalline polyolefin is good. For this purpose, an adhesion improver can be added to the matrix material and/or to the crystalline polyolefin.

The viscosity ( $\eta$ ) of the matrix material is an important parameter in the method according to the invention. Depending on the conditions under which the conversion of the crystalline polyolefin to fibrils takes place, the viscosity must have at least a minimum value  $\eta_{min}$  under the processing conditions, which value is determined from the equation:

$n_{\min} = \tau_{\min} / \gamma$

in which  $\tau_{\min}$  is the minimum shear stress for conversion to fibrils and  $\gamma$  is the rate of shear. The minimum shear stress  $\tau_{\min}$  depends on the crystalline polyolefin used. For UHMWPE this is approximately  $20-30 \times 10^{-4} \text{ N/m}^2$  at  $120^\circ\text{C}$ . The rate of shear  $\gamma$  depends on the equipment in which the conversion to fibrils takes place and on the setting of this equipment. The rates of shear to be achieved in various equipment are known to those skilled in the art. The rate of shear  $\gamma$  is, inter alia, dependent on the geometry of said equipment. In equipment in which high rates of shear occur, the viscosity of the matrix material can therefore be lower than in equipment in which the rates of shear remain low.

The following may be mentioned as examples of the matrix material: polyethylene, polypropylene, plasticised polyvinyl chloride or copolymers based on these polymers and rubbers; particularly suitable matrix materials are low density polyolefin (LDPE), linear low density polyolefin (LLDPE), very low density polyolefin (VLDPE), ethylene/vinyl acetate copolymers, ethylene/propylene/(third monomer) rubbers (EP(D)M rubbers) and styrene/butadiene rubber (SBR).

Reactive substances, such as, for example, vulcanising agents or 'crosslinking agents' can be incorporated in the matrix material. These reactive substances preferably have an activation temperature which is above the processing temperature of the matrix material. The activation temperature must, however, be below the melting point of the crystalline polyolefin.

The polymer compositions can be used in many applications which are known for reinforced polymer compositions, for example as construction material (mould sections, sheets, sections, pipes or hoses) in laminates or as films. Both rigid and flexible reinforced polymer compositions can be obtained according to the invention. An example of application of flexible reinforced polymer composition is the application in a tyre for automobiles, having increased puncture resistance.

A particular embodiment of the invention is that in which, after forming of the fibrils, the matrix material is separated from the fibrils. By selecting a suitable matrix material, the fibrils can be separated herefrom, loose fibrils of high tensile strength and rigidity being obtained. The loose fibrils can be used in various applications, as staple fibres. The separation of matrix material and fibrils can be carried out, for example, by dissolving or melting the matrix material.

According to the invention, fibrils is used to denote bodies having a length (L) which is large compared with the width and the thickness or the diameter (D). For a fibril, the L/D ratio is at least 4, preferably at least 10 and in particular at least 25. Fibrils of varying diameter and length are present in a polymer composition prepared according to the invention. Usually the dimensions of the fibrils are such that the said fibrils have a diameter of less than  $5 \times 10^{-4}$  m and a length of  $2 \times 10^{-3}$  to  $100 \times 10^{-3}$  m. Preferably, the fibrils have a diameter of less than  $3 \times 10^{-4}$  m, in particular less than  $1 \times 10^{-4}$  m. The particle size of the crystalline polyolefin from which the fibrils are prepared is of importance for the dimensions of the fibrils.

The temperature  $T_c$ , at which the crystalline polyolefin is converted into fibrils, must be higher than the processing temperature of the matrix material but lower than the melting point of the crystalline polyolefin.

The mixing of the crystalline polyolefin and the matrix material and the conversion to fibrils can take place in equipment suitable for applying shear stresses and for generating extensional flow. Preferably, high tensile stresses can be applied in this equipment to the polymer composition located in the equipment. Examples of such equipment are extruders and injection moulding machines, provided with conically tapered screw sections and/or Couette sections, rollers, and Brabender mixers.

Depending on the conditions during the formation of

th fibrils, it is possible, with th aid of the m thod according to the invention, to prepare anisotropic polymer compositions which are oriented in a specific direction and consequently have a higher ultimate tensile strength and modulus in this direction than in other directions.

The invention is illustrated below with reference to the following illustrative embodiments.

10

#### Example I

The matrix material used is an ethylene/vinyl acetate copolymer (EVA) which has a melt index (determined in accordance with ASTM standard D1238 at 190°C and with a load of 2.16 kg) of 0.2, of the ELVAX<sup>®</sup> 670 type from Du Pont. Crystalline high molecular weight polyethylene (polyolefin) is prepared in accordance with Example 5 of US-A-4769433. The crystalline polyethylene thus obtained has an intrinsic viscosity (I.V.) of 30 and a molecular weight (M<sub>w</sub>) of  $5.6 \times 10^6$ . The melting point is 142°C. The average particle size of the crystalline polyethylene particles is 900  $\mu\text{m}$ . The maximum stretch ratio of the polyethylene is 100. With the aid of a roller of the Collin 150 x 450 type (Walzwerk Dr Collin GmbH), a polymer composition is prepared from 90 g of matrix material and 10 g of crystalline polyolefin.

#### Rolling procedure:

The matrix material is processed on the roller at a rolling temperature of 110°C until a rolled sheet is formed. The speed of rotation of the two rolls of the roller is 10 revolutions per minute (no friction, RPM=10). After 2 minutes, the crystalline polyolefin is uniformly sprinkled over the rolled sheet. After waiting for 1 minute, the speed of revolution of one of the rolls of the roller is increased to RPM=20. The gap between the rolls is adjusted to 0.1 mm. After rolling for 3 minutes, the roller is stopped and the polymer composition form d is removed from the roller.

**Pressing:**

22 g of the polymer composition formed after the  
5 rolling procedure are pre-pressed at a temperature of 90°C  
and under a weight of 1,000 kg for 30 s in a mould for eight  
150 x 50 x 3.2 mm plates. The amount (22 g) is calculated  
from the total volume of the mould and the density of the  
polymer composition, a 5% excess being maintained. The  
10 polymer composition is then pressed at a temperature of  
120°C and under a weight of 50,000 kg for 7 minutes in the  
steel mould to a thickness of 3.2 mm, after which the shaped  
polymer composition is cooled at a rate of 40°C/minutes.

The determination of the ultimate tensile strength  
15 ( $\sigma$ ), the modulus (E) and the elongation at break ( $\epsilon$ ) of the  
polymer composition is carried out in accordance with ISO  
standard 37 type 2 on a test rod having a thickness of  
3.2 mm, at a pulling speed of  $20 \times 10^{-3}$  m/minute.

A fibre approximately 40 mm long is taken from the  
20 polymer composition and the tensile strength of said fibre  
is determined with the aid of a Zwick 1445 type tensile  
testing machine. A fibre 40 mm long is clamped in the clamp  
of the tensile testing machine over a clamping length (gauge  
length) of 20 mm. The pulling speed is adjusted to 0.5 times  
25 the clamping length per minute. The cross-section of the  
fibre is calculated from measured values for the length and  
the density of the fibre. The characteristics of the polymer  
composition are given in Table 1.

If the matrix material is processed as described  
30 above without crystalline polyolefin, a material is obtained  
which has an ultimate tensile strength  $\sigma$  of 20 MPa, a  
modulus E of 52 MPa and an elongation at break  $\epsilon$  of 928%.

**Example II**

35 A polymer composition is prepared as in Example I  
but in this case from 80 g of matrix material and 20 g of  
crystalline polyolefin. The results are given in Table 1.

Example III

A polymer composition is prepared as in Example I but in this case from 70 g of matrix material and 30 g of crystalline polyolefin. The results are given in Table 1.

Example IV

A polymer composition is prepared as in Example I but in this case from 60 g of matrix material and 40 g of crystalline polyolefin. The results are given in Table 1.

Table 1

Results of Examples I-IV: influence of the amount of UHMWPE (matrix material is EVA, rolling temperature 110°C)

Example	Amount of UHMWPE (% by wt.)	Fibril formation	Fibrils $\sigma_E$ (GPa)	Polymer composition $\sigma_E$ (MPa)	$\epsilon$ (%)
I	10	yes	1.8	31	10
II	20	yes	1.0	21	12
III	30	yes	1.5	31	12
IV	40	yes	1.3	20	17
				184	27

Examples V, VI and comparative Examples A and B

In Examples V and VI and comparative Examples A and B the influence of the processing temperature on the properties of the polymer composition obtained is investigated. A polymer composition is prepared as in Example I but in this case from 80 g of matrix material and 20 g of crystalline polyolefin. The rolling temperature is varied from 120-150°C for the various examples. The results are given in Table 2.

It is seen from this series of examples that if highly stretchable UHMWPE is processed above its melting point no fibril formation occurs.

Table 2

Results of Examples V and VI and comparative  
 5 Examples A and B: influence of rolling temperature (matrix  
 material is EVA; amount of UHMWPE 20% by weight).

Example	T <sub>roller</sub> (°C)	Fibril formation σ	Fibrils (GPa)	Polymer composition σ <sub>E</sub> (MPa)	E (MPa)	ε (%)
V	120	yes	1.9	23	11	153
VI	130	yes	1.7	26	12	165
A	140	no	-	-	7	60
15 B	150	no	-	-	7	62
						74

In comparative Examples C to G inclusive the  
 influence of the type of crystalline polyolefin on the  
 properties of the polymer composition obtained is  
 20 investigated. It is found that if UHMWPE which has a maximum  
 stretch ratio of less than 20 is used, no fibril formation  
 takes place below the melting point and above the melting  
 point (Example G) relaxation of the fibrils formed occurs,  
 25 as a result of which ultimately no fibrils are present in  
 the polymer composition.

#### Comparative Example C

A polymer composition is prepared as in Example I,  
 30 but using, as the starting materials, 80 g of ethylene/vinyl  
 acetate of the type Elvax<sup>®</sup> 670 as matrix material and 20 g  
 of crystalline polyethylene of the type Stamyian UH510 from  
 DSM. This crystalline polyethylene has a maximum stretch  
 ratio of 1. The melting point is 140°C. The roller  
 35 temperature is 120°C. The results are given in Table 3.

#### Comparative Example D

A polymer composition is prepared as in Example I  
 but using, as the starting materials, 80 g of ethylene/vinyl

acetate of the type Elvax<sup>r</sup> 670 as matrix material and 20 g of crystalline polyethylene of the type HIFAX 1900<sup>r</sup> from 5 Hercules. This crystalline polyolefin has a maximum stretch ratio of 16. The melting point is 142°C. The roller temperature is 120°C. The results are given in Table 3.

Comparative Example E

10 A polymer composition is prepared as in Example D but 20 percent by weight of decalin, calculated relative to the crystalline polyethylene, is added to the crystalline polyethylene of the type HIFAX 1900<sup>r</sup>. The roller temperature is 120°C. The results are given in Table 3.

15

Comparative Example F

A polymer composition is prepared as in Example E, but the roller temperature is 130°C. The results are given in Table 3.

20

Comparative Example G

A polymer composition is prepared as in Example I but using, as the starting materials, 80 g of ethylene/vinyl acetate of the type Elvax<sup>r</sup> 670 as matrix material and 20 g 25 of crystalline polyethylene of the type Stamylan UH210 from DSM. This crystalline polyolefin has a maximum stretch ratio of 1. The melting point is 142°C. The roller temperature is 150°C. The results are given in Table 3.

Table 3

Results of comparative Examples C-G: influence of  
5 type of UHMWPE. (\* = containing 20% by weight of decalin)

Example	Type of UHMWPE	T <sub>roller</sub> (°C)	Fibril formation	Polymer composition	σ (MPa)	E (MPa)	ε (%)
10	C UH510	120	no	7.4	64	575	
	D HIFAX1900	120	no	6.5	64	414	
	E HIFAX1900*	120	no	6.6	54	369	
	F HIFAX1900*	130	no	7.7	57	424	
15	G UH210	150	no	9.5	54	483	

Examples VII-IX

In Examples VII to IX inclusive, LDPE having a  
20 density of 0.921 kg/m<sup>3</sup>, of the type Stamylan 2101 TN04 from  
DSM, is used as matrix material. A polymer composition is  
prepared as in Example I, but using, as the starting  
materials, 80 g of LDPE as matrix material and 20 g of  
crystalline polyolefin of the type from Example I. In  
25 Examples VII to IX inclusive, the roller temperature is  
varied. The results are given in Table 4.

If the LDPE matrix material is processed as  
described above without crystalline polyolefin, a material  
is obtained which has an ultimate tensile strength (σ) of 12  
30 MPa, a modulus (E) of 121 MPa and an elongation at break (ε)  
of 915%.

Table 4

Results of Examples VII-IX: influence of the roller  
 5 temperature (matrix material = LDPE; 20% by weight of  
 UHMWPE)

Example	T <sub>roller</sub> (°C)	Fibril formation	Fibrils σ (GPa)	Polymer E (GPa)	composition σ (MPa)	E (MPa)	ε (%)
VII	130	yes	0.7	13	10.2	252	31
VIII	120	yes	1.2	25	19.6	335	27
IX	110	yes	1.2	24	7.9	94	92

15

Examples X and XI and comparative Examples H, J and K relate to mixtures in which the matrix material is a rubber. The results are given in Table 5.

20

#### Example X

(A) Using a simultaneously rotating twin-screw extruder, a suspension of 15% by weight of UHMWPE of the type HB 312 from Himont, having a weight-average molecular weight of  $1.5 \times 10^6$  kg/kmol is converted to a homogeneous solution in decalin at about 180°C. The solution is extruded as a plane sheet having a thickness of 1.0 mm and cooled until a gel forms. After evaporating the decalin, the sheet formed is ground to a fine powder having an average particle size of 900 µm. The crystalline polyolefin powder obtained has a maximum stretch ratio of 43.

(B) 10% by weight of the powder obtained in the above manner is added to an ethylene/propylene/diene rubber (EPDM) compound of the type Keltan 512 x 50 from DSM. Using this compound, a mixture is prepared in accordance with ISO 4097-1980(E), which mixture is then rolled for 5 minutes at 120°C using the rolling procedure as described in Example I, UHMWPE fibres being formed. After rolling, one part by weight of vulcanising agent of the type Rhenocure AT from

Rheinau GmbH is mixed rapidly with 272 parts by weight of the compound, after which the latter is vulcanised for 30 minutes at 120°C.

Example XI

A compound which contains 20% by weight UHMWPE in EPDM is prepared as in Example X.

10

Comparative Example H

A compound is prepared as in Example X under (B), using UHMWPE of the type HB 312 from Himont directly as the starting material, without pre-processing via a solution.

15 The UHMWPE has a maximum stretch ratio of 1.

Comparative Example J

A compound is prepared as in Example X, except that vulcanisation takes place at 160°C.

20

Comparative Example K

A compound is prepared as in Example X under (B), but without UHMWPE.

25 Table 5

Results of Examples X and XI and comparative Examples H, J and K (matrix material is ethylene/propylene/diene rubber):

30 Example via Amount of Vulcanisation Polymer composition

		solution	UHMWPE (% by wt)	temperature (°C)	$\sigma$ (MPa)	E (MPa)
	X	yes	10	120	78	5.4
35	XI	yes	20	120	95	7.2
	H	no	10	120	45	3.1
	J	yes	10	160	50	7.8
	K	-	0	120	42	1.9

It follows from the results that polyethylene processed via solution, which has a maximum stretch ratio of 43, gives a great improvement in the ultimate tensile strength and modulus of elasticity. If the polymer composition is vulcanised at a temperature of 160°C, that is to say above the melting point of the polyolefin, the ultimate tensile strength remains much lower.

C L A I M S

- 5 1. Method for the preparation of a reinforced polymer composition which contains fibrils of a crystalline polyolefin having a weight-average molecular weight  $M_w$  of at least  $5 \times 10^5$  kg/kmol, particles of the crystalline polyolefin being converted into fibrils in a matrix material which is immiscible with the crystalline polyolefin, characterised in that the crystalline polyolefin has a maximum stretch ratio of at least 20 and the conversion to fibrils takes place at a temperature below the melting point of the crystalline polyolefin.
- 10 2. Method according to Claim 1, characterised in that the crystalline polyolefin has a weight-average molecular weight  $M_w$  of  $1 \times 10^6$  to  $10 \times 10^6$  kg/kmol.
- 15 3. Method according to Claim 1 or 2, characterised in that the crystalline polyolefin is polyethylene, having a maximum stretch ratio of at least 40.
- 20 4. Method according to Claim 3, characterised in that the crystalline polyolefin has a maximum stretch ratio of at least 80.
- 25 5. Method according to Claims 3 or 4, characterised in that the crystalline polyethylene has a DSC melting point of at least 140°C.
- 30 6. Method according to one of Claims 1-5, characterised in that the crystalline polyolefin has a crystallinity of at least 80%.
- 35 7. Method according to one of Claims 1-6, characterised in that the matrix material consists of a thermoplastic rubber.
8. Method according to one of Claims 1-6, characterised in that the matrix material consists of a low density polyolefin (LDPE).
- 35 9. Reinforced polymer composition obtainable using the method according to one of Claims 1-8.
- 40 10. Fibrils obtainable using the method according to one of Claims 1-8, after separating off the matrix material.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/NL 91/00061

## I. CLASSIFICATION & SUBJECT MATTER (if several classification symbols apply, indicate all).<sup>1</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

**IPC:** 5 C 08 J 5/04; D 01 F 8/06, C 08 J 5/18

## II. FIELDS SEARCHED

Minimum Documentation Searched.<sup>2</sup>

Classification System	Classification Symbols
IPC <sup>5</sup>	D 01 F, C 08 J

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched.<sup>3</sup>

## III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>4</sup>

Category <sup>5</sup>	Citation of Document, <sup>6</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
Y	EP, A, 0106764, (SOCIETE CHIMIQUE DES CHARBONNAGES) 25th April 1984 see the claims. -----	1-9
Y	US, A, 4123476 (A. BONNEFON et al.) 31st October 1978, see claims & DE, A, 2418803 cited in the application -----	1-9
A	EP, A, 0043288 (BXL PLASTICS LTD) 06th January 1982 -----	
A	FR, A, 2387115 (UBE INDUSTRIES LTD.) 10th November 1978 see claims -----	1
A	EP, A, 0260974 (THE DOW CHEMICAL COMPANY) 23rd March 1988 -----	./.

### \* Special categories of cited documents:<sup>10</sup>

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the International filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

10th July 1991

Date of Mailing of this International Search Report

16.09.91

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

Falk Heck

## III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	US, A, 3546063 (A.L. BREEN) 08th December 1970 see claims; column 7, lines 46-49	10
A	EP, 0322838 (TEIJIN LIMITED) 05th July 1989	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO. NL 9100061**  
SA 46642

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 30/08/91. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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